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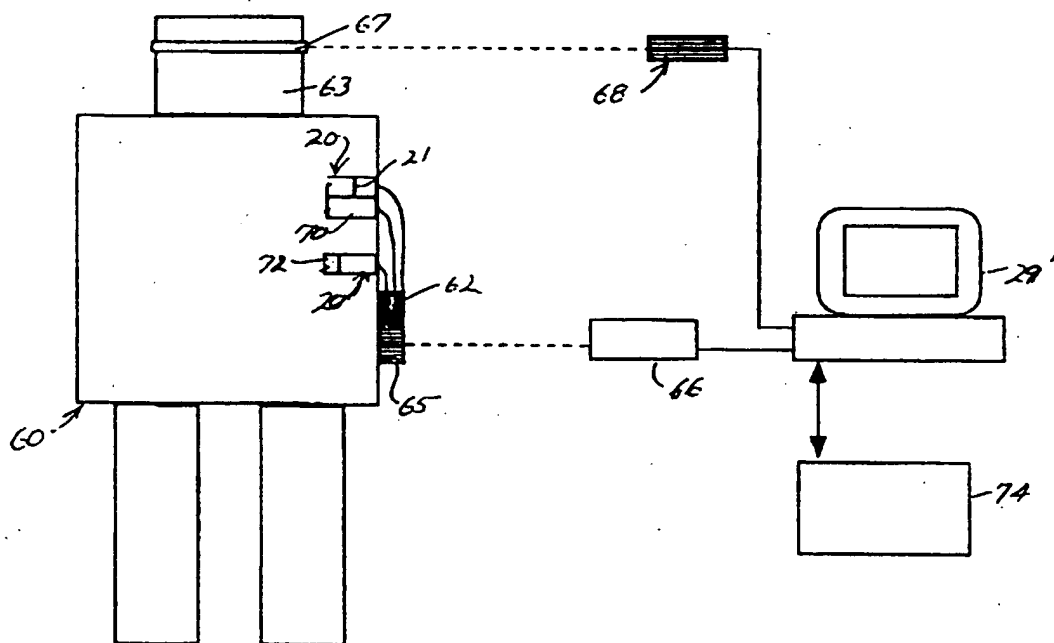
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(54) **METHODE ET INSTRUMENT DE DETECTION ET DE MESURE  
DE FAIBLES NIVEAUX DE GAZ POUVANT ETRE UTILISES  
DANS LA DEFENSE CONTRE PRODUITS CHIMIQUES ET LA  
SURVEILLANCE DE L'ENVIRONNEMENT**

(54) **A METHOD AND INSTRUMENT FOR DETECTION AND  
MEASUREMENT OF LOW LEVELS OF GASES WITH  
APPLICATIONS IN CHEMICAL DEFENSE AND  
ENVIRONMENTAL MONITORING**



(57) A method and system for determining concentrations of gases in an unknown gas mixture using stored data voltage profiles obtained by measuring such profiles of known gases.

ABSTRACT OF THE DISCLOSURE

A method and system for determining concentrations of gases in an unknown gas mixture using stored data voltage profiles obtained by measuring such profiles of known gases.

A Method and Instrument for Detection and Measurement  
of Low Levels of Gases with Applications in Chemical Defense  
and Environmental Monitoring

BACKGROUND OF THE INVENTION

5 Field of Invention

The invention relates to an instrument for measuring the concentration of a gas, or several gases, present in low concentrations in a gas mixture. More particularly, the invention relates to an instrument, incorporating a gas sensor,  
10 or a plurality of gas sensors, for measuring the concentration of gases used as simulants for chemical warfare agents, or for measuring the actual agents (live agents), in the field, the laboratory, or within suits designed to protect wearers from toxic gases. The instrument differs from previous analyzers of  
15 chemical warfare simulants in that it allows continuous measurement of gases in real time, it is extremely compact and may be battery operated. Unlike other gas analyzers, the instrument may be housed directly within a chemical warfare suit.

The invention also relates to a method by which signals from  
20 a plurality of gas sensors can be deconvoluted in software to provide the most likely composition of a gas mixture. The method involves the measurement of individual gases by the sensors to obtain a voltage profile for each gas, and the construction of a library of voltage profiles for a number of gases. The software  
25 compares a measured voltage profile from a gas mixture to the voltage profiles in the library, and determines the most likely

combination of gases in the sample.

As well as defense applications, the instrument and gas analysis method can be used to determine gas concentrations in pure and mixed gases sampled from any environment . Obvious applications include monitoring of industrial and domestic gas supplies, and atmospheric monitoring for environmental studies.

#### Brief Description of the Related Art

Use of chemical warfare agents in the Gulf War, and the increasing potential for use of such agents in terrorist attacks, have prompted the development of new materials for use in chemical defensive clothing. Part of the development requires the testing of suit material for permeation of chemical agents, and involves, among other tests:

(1) Application of the agent to one side of a sample of suit material and measurement of the amount of agent that permeates to the other side of the sample. This is called a breakthrough test.

(2) Exposure of persons wearing chemical warfare suits to gaseous chemicals in a test chamber, and measurement of permeation of those chemicals through the suit. This is called a MIST test.

In the early stages of such testing, simulants rather than the actual chemical warfare agents (live agents) are used. Simulants have similar permeant properties to the live agents,

but are not toxic at the concentrations used. Methyl salicylate is commonly used in tests as a simulant compound. The purpose of the tests is to determine the conditions under which gases may leak through the suits, and the concentration of gas that results within the suit when a breakthrough occurs.

A diagram of the type of apparatus 12 used in the breakthrough test is shown in Fig.1. A piece of suit material 13 is placed in a sample chamber 14 so that the material separates the chamber into an upper 15 and a lower section 16. The outer surface 13A of the suit material is exposed to the upper part of the chamber, and the inner part 13B of the material is exposed to the lower part of the chamber. A test gas 17 at a known concentration is flushed through the upper part of the chamber, and gas samples are removed from the lower part of the chamber for analysis through sampling port 18. Alternatively, droplets of a compound may be placed on the outer surface of the suit material and vapors from this compound permeating the fabric may be sampled from the lower side of the chamber for analysis. Ideally, in breakthrough tests the kinetics of gas permeation through the material should be measured so that the time at which breakthrough occurs is known, as well as the rate of movement of gas through the material. However, this requires continuous monitoring of the gas phase in the lower part of the chamber by extremely sensitive gas detection instruments. Unfortunately, the most sensitive instruments, such as gas chromatographs, require several minutes to measure a single sample so continuous

monitoring is not possible. Obviously, there is a need for sensitive gas sensors that can make continuous measurements of gas concentrations in breakthrough tests.

5 In MIST tests a compound such as methyl salicylate is vaporized and pumped through the MIST chamber at a known rate containing a person dressed in a chemical warfare suit. The concentration of methyl salicylate within the chamber is monitored continuously using an infra-red gas analyzer set at an appropriate wavelength for detection. To obtain very accurate  
10 measurements of methyl salicylate in the low part per million and part per billion range, a gas chromatograph is used. This involves taking a sample of gas from the chamber and injecting it into the gas chromatograph which separates the methyl salicylate from other air components and measures the methyl salicylate  
15 peak. This procedure requires approximately 6 minutes between samples and therefore provides only intermittent measurement of methyl salicylate concentration in the chamber.

Before donning the suit and entering the chamber, the test subject attaches patches of material to his or her skin which  
20 contain a compound, Tenex TA (Supelco Corp.), that absorbs methyl salicylate. The Tenex TA is sealed beneath a membrane that has similar permeant properties to human skin so that the amount of methyl salicylate absorbed by the Tenex TA is similar to the amount of methyl salicylate entering the subject's body over the  
25 area of the patch. After the subject has been exposed to a known concentration of methyl salicylate for a known period, the

subject leaves the test chamber, removes the suit, and removes the patches from the skin. The Tenex TA is then desorbed and methyl salicylate released is trapped in a solvent. The concentration of methyl salicylate in the solvent is then  
5 analyzed using high performance liquid chromatography (HPLC).

The MIST test has several serious flaws. Most important, the methyl salicylate is not measured continuously within the suit, so the time at which permeation occurs and the rate at which methyl salicylate accumulates within the suit are not  
10 known. Also, the detection systems for methyl salicylate are large, cumbersome and expensive. A Miran infra red gas analyzer is most commonly used for the MIST test. This is manufactured by Foxboro Corporation of East Bridgewater Mass., measures approximately 42 x 80 x 24 cm, weighs approximately 20 kg, and  
15 costs approximately \$18 000 US. The Minicam is the most compact, and least expensive gas chromatograph for detection of methyl salicylate but this measures approximately 40 x 40 x 40 cm, weighs approximately 10 kg and costs approximately \$27 000 US. Various HPLC instruments may be used for detection of methyl  
20 salicylate from skin patches, and all are large-scale lab-based instruments that cost upward of \$20 000 US.

Ideally, the methyl salicylate permeation tests should be carried out using a sensor that can be contained within the suit, so that real-time measurement of methyl salicylate permeation can  
25 be monitored. Obviously, this is not possible with the infra red, gas chromatograph or HPLC instrumentation currently

available. Also, it is the eventual goal of military and civilian defense organizations to incorporate chemical warfare agent detection sensors into every suit issued to their personnel to provide warning of permeation under field conditions.

5 Therefore, the sensors must be portable, preferably battery-operated, and inexpensive, as well having the sensitivity necessary for low-level chemical agent detection. In this patent document we describe a device that measures methyl salicylate at levels at or below those detectable by the Miran infra red gas  
10 analyzer, has a volume of less than 10 cm<sup>3</sup>, weighs approximately 10 g, and is very inexpensive to manufacture. The sensor may be battery-operated, and could be used within a chemical warfare suit.

Different chemical warfare agents may be used in  
15 combination, and tests of suit materials may involve mixtures of gases as well as individual compounds. A very useful attribute of a gas analysis instrument would be the ability to measure the concentrations of specific gases in a gas mixture. This is particularly important when using a sensor within a suit worn by  
20 a test subject, since the human body produces many gases from the skin, the gastro-intestinal tract and respiratory tract that may affect the atmosphere within the suit. In this patent document we describe a method by which signals from several different gas sensors may be used to determine the concentration of individual  
25 gases in a gas mixture.

A multi-sensor gas analyzer for detection and measurement of



individual gases within a gas mixture has numerous applications for both defense use and environmental monitoring. The small size of the sensors allows several to be incorporated into a chemical warfare suit. The voltage outputs from these can be sent by telemetry to a central computer where their combined signals can be deconvoluted, and the atmosphere within the suit analyzed. In addition the sensors can be incorporated into a separate gas analysis instrument capable of sampling gas from any environment, and analyzing its constituents. Such an instrument could be battery-powered for use in the field and could determine the atmospheric levels of chemical warfare agents in field conditions.

#### Summary of the Invention

Disclosed is an instrument for the continuous monitoring of individual gases, or gas mixtures, used in testing fabrics for chemical defense clothing, either in a breakthrough test, or in a MIST test. In a preferred embodiment of the invention a solid-state gas sensor is used that contains a ceramic semi-conductor element that is heated to provide a surface on which test gases are oxidized. This oxidation causes a change in the electrical conductivity of the semi-conductor proportional to the concentration of oxidizable gas to which it is exposed. Sensitivity and selectivity of the instrument depends on the chemical nature of the ceramic semi-conductor, and on the

temperature to which it is heated. In addition, a membrane selective only for the gas of interest may be placed in front of the sensor, so that only this gas reaches the sensing element. In an alternative embodiment of the invention several sensors are used that produce different voltage outputs in the presence of different oxidizable gases. The output from these sensors provides a specific voltage profile for each gas. Disclosed is a method by which these voltage profiles may be stored in a software library and compared to the voltage profile obtained when a specific complement of sensors is exposed to a test gas or a gas mixture. The software can then deconvolute the measured voltage profile and provide a measurement of the concentration of the compound, or compounds, in the test gas.

According to a first aspect of the invention, a device is disclosed for continuous measurement of concentrations of a gas within an article of clothing such as a suit or gas mask of a type designed to provide a barrier between a user and the gas. The device includes at least one portable gas sensor having an output, a portable means for supplying power to the at least one gas sensor, and means for monitoring the output from the at least one gas sensor to provide a continuous measurement of the concentrations of the gas.

According to another aspect of the invention, a method is disclosed by which the concentration of a gas, or the concentrations of a plurality of gases in a gas mixture, is measured. The method includes the steps of exposing a plurality

of first gas sensors to a plurality of known gases to obtain voltage outputs from the sensors that together represent specific voltage profiles for each gas, storing the voltage profiles as a library in a software program, exposing a plurality of second gas  
5 sensors to an unknown gas of unknown specific composition and measuring the voltage outputs from the plurality of second gas sensors to provide a voltage profile for the unknown gas, and using the software program to compare the voltage profile of the unknown gas to the voltage profiles of known gases in the  
10 library, and thereby determining the concentration of a specific gas or gases, in the unknown gas.

According to a further aspect of the invention, a method is disclosed by which the concentration of an unknown gas, or the concentrations of a plurality of unknown gases in an unknown gas  
15 mixture, is measured within an article of protective gear. The method includes the steps of providing at least one gas sensor within the article of protective gear so that the at least one gas sensor is exposed to the unknown gas within the protective gear, providing a voltage output from the at least one  
20 sensor, and conveying the voltage output from the at least one gas sensor to a data acquisition system so as to compare the voltage output with data retained within the data acquisition system in order to define the unknown gas.

According to a further aspect of the invention, a device is  
25 disclosed for measuring concentrations of gases in a gas or gas mixture. The device includes a housing and a plurality of gas

sensors mounted within the housing. Each of the gas sensors includes a ceramic sensing element. Electrical circuit means connect each of the sensing elements to a source of power supply and connect an output from each of the sensing elements to a data acquisition system. A gas inlet is provided into the housing such that gas enters the housing and into communication with the sensing elements and a gas outlet is provided from the housing. Means are also provided for conveying the gas from the inlet to the outlet of the housing.

10 Brief Description of Drawings

Fig. 1 shows an apparatus used in breakthrough tests of fabric according to prior art.

Figs. 2A and 2B, show structures of a ceramic gas sensor according to prior art.

15 Fig. 3 shows an electronic circuitry for ceramic gas sensor according to prior art.

Fig. 4 shows a gas delivery system used to assess response of sensors to organic vapors

20 Fig. 5 shows a response of 10 gas sensors to low concentrations of toluene, octane, 1,4 dichlorobutane, hexanol and methyl salicylate.

Fig. 6 show a time course of response of sensors TGS 813 and TGS 826 after exposure to 180 ppm toluene.

Fig. 7 shows calibration curves for 10 gas sensors at

different concentrations of 1,4 dichlorobutane.

Fig. 8 shows a flow-through instrument for gas detection incorporating a TGS 826 ceramic gas sensor.

Fig. 9 shows a comparison of the responses to increasing concentrations of methyl salicylate between an instrument incorporating a flow-through TGS 822 gas sensor, and a Miran infra red gas analyzer.

Fig. 10 shows a system for investigating permeation of vapors through fabrics incorporating a flow-through gas sensor.

Fig. 11 shows a multi-sensor gas analyzer for the measurement of individual gas concentrations in gas mixtures.

Fig. 12 shows a system for real time measurement of gas concentrations within a suit or gas mask with RF link between sensor and computer.

#### Description of the Preferred Embodiment

One embodiment of the invention incorporates a single gas sensor for measuring gases that may be used as chemical warfare agent simulants or live agents. The sensor is non-specific and can measure the concentration of several different gases, provided that each is used in a separate test, and the sensor is calibrated against a range of concentrations of the gas before the test is initiated.

A preferred type of gas sensor 20 (see Fig. 2) used in the test system contains a ceramic sensing element 21 formed on an alumina ceramic tube. Such sensors are commercially available

from Figaro Engineering Inc. of 1-5-3 Senbanishi, Mino, Osaka 562 Japan, distributed in the United States by Figaro USA Inc. of PO Box 357, Wilmette IL 60091. Alternative manufacturers include Scimarec Co. Ltd of 14-1 Nishi-Shimbashi, 2-Chone, Minato-ku, Tokyo 101 Japan, distributed in the United States by Voltronics Sensors Corp., 100 Ford Road, Denville, NJ 07834. Both of the above-mentioned manufacturers provide a range of sensors that are designed for detection of a range of gases including Hydrogen, Carbon Monoxide, Methane, Propane, and Butane, and well as vapors such as those from gasoline and ethanol. These sensors are used in air quality control systems, but have not been used in instruments for the detection of chemical warfare simulants or live agents.

All sensors are extremely compact and include a housing measuring 1.7 to 2.5 cm in diameter with a depth, including pin connections to the electronic circuitry (Fig. 3), of 1.7 to 2.3 cm (Fig. 2). The sensing element consists of a ceramic that may consist of tin dioxide or tungsten oxide, and this is heated to approximately 400° C by an internal heater coil. Gases diffuse through a metal grid that acts as a flame arrester and are oxidized on the surface of the ceramic sensing element. This changes the conductivity of the element in proportion to the concentration of the gas that is being oxidized. The measuring or electrical circuit for a typical ceramic gas sensor is shown in Fig. 3. A regulated 5 VDC power supply is required for the heating coil, and this is also used to set up a voltage

divider between the sensing element and an external resistance. This resistance can be varied by a potentiometer 28 to change the signal output span of the sensor for use across different gas concentration ranges. The entire electronic circuitry, excluding  
5 power supply can be housed in a volume less than that of the sensor itself. If size is important, the power can be supplied by a compact 5V battery. The sensors cost between \$15 and \$60 US, and the circuitry required for their function is inexpensive. Therefore the sensors are much less expensive, and far more  
10 compact, than other devices (e.g. gas chromatographs and infra red gas analyzers) for the measurement of chemical warfare simulants and live agents.

We have shown that several of the gas sensors manufactured by Figaro Engineering Inc. can measure the concentrations of a  
15 number of gases used as simulants of chemical warfare agents. The concentrations of simulants used in these tests were typical of those used in breakthrough tests of chemical warfare suit fabric, and for monitoring the concentration of methyl salicylate used in MIST chamber tests.

20 The sensors we used include those shown in Table 1 below.. However, it will be appreciated by those skilled in the art that other ceramic sensors may also respond to simulants and live agents.

TABLE 1: FIGARO GAS SENSORS AND THEIR TARGET COMPOUNDS

SENSOR NUMBER	TARGET GAS(ES) RECOMMENDED BY FIGARO INC.
TGS 822	Alcohol, toluene, xylene, organic solvents
TGS 880	Volatile gases and water vapor from food
TGS 821	Hydrogen
TGS 842	Methane
TGS 813C	General combustible gases
TGS 830	Chloroflurocarbons
TGS 813	General combustible gases
TGS 826	Ammonia
TGS 800	Air contaminants (especially cigarette smoke)
TGS 825	Hydrogen Sulphide

To determine the sensitivity and specificity of the sensors 21 for different simulants, a flow-through gas sensor block 30 was constructed in which the 10 (ten) sensors listed above were housed (Fig. 4). The block was constructed of Teflon since this is extremely impermeable to most organic vapors, and resists plaquing of compounds such as methyl salicylate. Methyl salicylate has a tendency to bind to most materials. The block measured 14.0 x 6.0 x 3.5 cm and had an internal gas volume of approximately 260 cm<sup>3</sup>. The sensors were aligned in two rows each consisting of five sensors. Only the sensing head 21' of each sensor was exposed to the air space 31 of the block and gases moved into these by diffusion. Electronic controls 32 and the power supply 33 were external. The block was connected to a gas mixing system 34 constituting two mass flow controllers 35 and 36. One of these 35 regulated the flow of air through a pure solution of the simulant 37 to create a flow of vapor, and the other 36 controlled the flow of compressed air from a supply 38



which was used to dilute the vapor to a known concentration. A pump 39 drew the diluted vapor through the chamber and across the sensing heads of the 10 sensors. Output from the sensors was monitored in real time by a computerized data acquisition system

5 29.

The simulants used in the study included toluene, octane, 1,4 dichlorobutane, hexanol and methyl salicylate. The response of each sensor to each of the gases is shown in Fig. 5. All sensors except TGS 821 produced a significant voltage output with

10 at least 4 of the 5 test gases, and most sensors showed a significant response to all gases. Surprisingly, TGS 826 which is marketed as an ammonia sensor, and TGS 825 which is marketed as a hydrogen sulphide sensor, showed the greatest outputs when exposed to the organic test gases, despite being marketed for

15 detection of inorganic gases.

The response of the sensors to the test gases was rapid, all showing a response within seconds of the gas entering the block. Fig. 6 shows the time course of the response of sensors to TGS 813 and TGS 826 when 180 ppm toluene was flushed through the

20 block. In both cases, 90% of the total response to the gas occurred within 60 seconds of exposure. A similar response time was observed in all other sensors that responded to toluene. This type of rapid, continuous response to gas exposure is essential in breakthrough tests of suit fabric because it

25 provides a measurement of the exact time at which breakthrough occurs, and allows analysis of the kinetics of gas movement

through the fabric. Such measurements are not possible with current methods of gas analysis used in breakthrough tests.

Calibration of the sensors showed that a power curve relationship exists between voltage output and the concentration of the test gases. This relationship is illustrated in Fig. 7 which shows the calibration data for 10 sensors at different concentrations of 1,4 dichlorobutane. The calibration data for each sensor may be linearised simply by plotting the natural log of the gas concentration against the natural log of the sensor voltage output. This allows for easy calculation of gas concentration when using data acquisition software to monitor gas sensor output.

An instrument containing a single sensor 21 for the detection of chemical warfare agent simulants was constructed using the TGS 826 sensor, although any sensor that shows a response to oxidizable gases may be used. The instrument 40 is shown in Fig. 8 including a housing 41. The sensor is modified from its initial form shown in Fig. 2, in which gases diffuse to the sensing element, by incorporating a luer-lock gas fitting inlet 42 into the flame arrester 25. This allows gases to be pumped directly past the sensing element so that the sensor does not have to be housed in a separate gas chamber. A membrane permeable only to the gas(es) of interest 43 may, if required, be incorporated in front of, or into, the gas inlet port, to increase the specificity of gas detection by the sensor. Gases entering the sensor head vent through a plastic housing

containing the electronic circuitry 26 for sensor function (shown in Fig. 3). A gasket 44 between the sensing element and the electronic circuitry housing prevents leakage of gases into or out of the instrument. The entire sensing unit 40 measures only 10 cm in length, and has a maximum diameter of 3 cm. Power is provide by a 5 VDC 3 Amp power adapter 45. This instrument has been tested at the Royal Military College of Canada, Kingston, Ontario which has a MIST chamber. A pump 46 was attached to the outlet 48 of the gas detector, and this sampled the atmosphere within the MIST chamber through a port. At the same time, the atmosphere was measured by a Miran infra red gas analyzer, and a Minicam gas chromatograph.

After a zero baseline was established methyl salicylate was introduced gradually into the chamber so that the concentration rose from zero to approximately 12 ppm. Throughout this rise, the gas detector incorporating the TGS 826 sensor, and the Miran infra red gas analyzer monitored the methyl salicylate concentration continuously. The Minicam gas chromatograph took discrete samples of chamber gas and was only able to provide a concentration reading every 10 minutes. As shown in Fig. 9, the output from the Miran infra red gas analyzer was tracked by the output from the TGS 826 sensor, showing that this simple, compact, inexpensive device can be used to replace a much more complex, expensive and unwieldy gas measuring system.

It will be appreciated that the gas measuring device 40 incorporating the TGS 826 sensor may also be used effectively in

breakthrough tests of suit fabric simply by incorporating the sensor into the portion of the breakthrough chamber in contact with the inside of the suit fabric. The sensor may be used directly in the chamber in its original diffusion-based operating mode, or a flow-through sensor of the type shown in Fig. 8 may be used with the breakthrough chamber as shown in Fig. 10 by connecting the sampling port 18 by way of tube 50 to the inlet port 42 of the instrument 40. The latter style of sensor may provide a better response time for gas detection.

Although the multi-sensor gas analyzer may be used as a laboratory-based instrument for detection of gases used in MIST tests and fabric breakthrough tests, the same concept may be applied to a plurality of sensors incorporated into a chemical warfare suit. The sensors need not be housed in a sensor block but could be placed in close juxtaposition within the suit to sample the internal atmosphere by diffusion.

It will also be appreciated that the small size of the gas detector shown in Figs. 2A, 2B and 3 would allow one, or a plurality of such detectors, to be placed within a suit 60, see Fig. 12, designed to protect the wearer from chemical warfare agents. These detectors would operate in diffusion-based mode, and would be powered by a single battery-pack power supply 62 which may be worn or carried exteriorly of the suit. The sensors could be placed in areas of the suit that are most prone to break-through, such as seams that are continually placed under stress. They could also be placed in gas masks 63 to ensure that

the masks are functioning effectively. Output from the sensors is transmitted by a RF transmitter 65 that forwards signals to a receiver 66 connected to a central computer 29'. If the output of any sensor were to reach a critical threshold limit the wearer could be alerted to the danger of gas exposure by a triggered alarm 67 which receives signals from a transmitter 68. As opposed to RF signals, an appropriate cable may be used to connect the sensor to the data acquisition system or computer 29'.

The power supply required for the sensors is compact, and they could be operated from a single 5V battery pack. Output from the sensors sent to the computer 29' is processed using deconvolution software 74 using data developed by predetermined tests and samplings as discussed elsewhere herein. The computer would provide continuous measurements of the concentrations of oxidizable gases within the suit. Neither the sensors, nor the power supply, would add significantly to the weight or the bulk of the suit, and would not restrict the wearer significantly. No other gas measuring device used currently for the detection of chemical warfare agents, or their simulants, has the portability and compactness required for use within a chemical warfare suit.

A problem with the use of sensors within a suit is that output of all sensors is affected by water vapor concentration. However, the output changes in a predictable manner and calibration of the sensors can be conducted at different relative humidities to establish a multiple regression relationship

between sensor voltage output, relative humidity and gas concentration. Measurement of relative humidity within the suit can be easily monitored by a simple humidity sensor 70. For example Hy-Cal Engineering of 9650 Telstar Ave., El Monte CA 5 91731, manufactures a humidity sensor with an integrated temperature sensor to correct readings for temperature fluctuations. The sensor has a volume of less than 1 cm<sup>3</sup> and weighs only 1.3 g. One or several of these sensors could be placed in close juxtaposition with the gas detectors in the suit, 10 and could be powered from the same power supply. Alternatively, a drying agent such as magnesium perchlorate could be placed in a small, gas porous column 72 sealed to the housing of the gas sensor in such a way that gases would diffuse through the drying agent before reaching the sensing element. Sensors could then be 15 calibrated under standard dry-gas conditions and humidity within the suit would not affect sensor output. The drying agent would require occasional replenishment when the suit is in use.

Ceramic gas sensors such as those manufactured by Figaro Engineering Inc. have high sensitivity but low selectivity, as 20 evidenced by the data shown in Fig. 5. Low selectivity poses a potential problem when the sensors are used in environments that contain a mixture of oxidizable gases. For example, chemical warfare agents used aggressively may be released in combination and it may, therefore, be advantageous to test suit materials 25 with a combination of simulants. Also, the atmosphere within a chemical warfare suit may contain a mixture of natural oxidizable

gases produced by the wearer, since these are released from the skin, the gastro-intestinal tract and the respiratory tract. In many experimental and practical-use situations it may be important to distinguish the levels of several different gases present in the external and internal atmosphere of the suit, or gases to which suit fabric is exposed. To this end, a multi-sensor gas analyzer 50 has been developed that incorporates the ten gas sensors listed in Table 1.

A diagram of the analyzer is shown in Fig. 11. It incorporates a flow-through gas chamber similar to that used to determine the characteristics of the sensors and shown in Fig. 4. The chamber is constructed of Teflon, measures 10.0 x 2.0 x 4.0 cm and has an internal gas volume of approximately 50 cm<sup>3</sup>. The sensors are aligned in two rows each consisting of five sensors. Only the sensing head of each sensor is exposed to the air space of the chamber and gases move into these by diffusion. The chamber is housed in a case 52 that contains a DC linear 5V 3Amp power supply 33. The case also houses the electronic circuitry 26 required for each sensor, including potentiometers 28 for controlling sensor output across different gas concentration ranges. The potentiometers range from 0 to 100 kiloOhm and are adjusted by dials 54 on the front panel of the analyzer. The front panel also incorporates gas inlet 55 and outlet ports 56 attached to Teflon tubing 57 and 58 for gas delivery to and removal from the sensor block 30. A pump is required to deliver gases to the sensor block, and this may be attached to the inlet

or the outlet tubing to push or pull gases through the analyzer. Each sensor produces a 0 - 5V analog output that may be recorded by an analog recording device or by data acquisition software via an analog to digital converter.

5        Although most of the sensors within the analyzer produce a voltage output when exposed to most oxidizable gases, the analyzer can be used to determine the concentrations of individual oxidizable components of a gas mixture through use of deconvolution software. As shown in Fig. 5, each sensor has a  
10       different voltage output when exposed to the same concentration of a combustible gas. By measuring the outputs of the sensors in the presence of individual gases, a ratio of the voltage outputs of the sensors can be obtained that represents a unique "voltage profile" for each gas. Such voltage profiles are stored as a  
15       library in software so that when the sensors respond to a mixture of gases, the overall voltage profile can be deconvoluted in software, and the most likely mixture of gases and their concentrations determined.

      Although the analyzer described above incorporates a sensor  
20       block with ten sensors, it will be appreciated that any number of different sensors may be used in the block, so that voltage profiles may consist of greater or lesser number of data points. Also, a specific complement of sensors may be used for specific applications of the analyzer. For example, one complement of  
25       sensors may be used to detect chemical warfare agents, while a different complement of sensors may be used for detection of



oxidizable gases in industrial or domestic situations. In each case the deconvolution software would access only the stored voltage profiles appropriate to the complement of sensors currently in use.

5           This novel approach to gas analysis has not been attempted previously, but is analogous to that used for determination of compounds in solution by spectrophotometric analysis. In such  
10           analyzes the absorbance spectrum of individual compounds is stored in a library. The deconvolution software compares the overall absorbance spectrum of a mixed solution to the spectra in  
15           the library and determines the most likely combination, and concentration, of components present. The absorbance spectra of the individual solutes in the spectrophotometric analysis is  
15           analogous to the voltage profiles of individual gases in the gaseous analysis.

          The foregoing description of the preferred embodiment of the invention has been presented to illustrate the principles of the invention and not to limit the invention to the particular  
20           embodiment illustrated. It is intended that the scope of the invention be defined by all of the embodiments encompassed within  
20           the following claims and their equivalents.

## WE CLAIM:

1. A device for continuous measurement of concentrations of a gas within an article of clothing such as a suit or gas mask of a type designed to provide a barrier between a user and the gas comprising, at least one portable gas sensor having an output, a portable means for supplying power to said at least one gas sensor, and means for monitoring said output from said at least one gas sensor to provide a continuous measurement of the concentrations of the gas.

2. The device of claim 1 wherein said at least one gas sensor contains a ceramic sensing element on which said gas is oxidized.

3. The device of claim 2 wherein said at least one gas sensor includes a housing in which said sensing element is retained, said housing defining a gas flow path to said sensing element, electronic circuitry mounted within said housing and electrically connected to said at least one sensor, and means for sealing of said electronic circuitry within said housing to prevent ingress of atmospheric gas.

4. The device of claim 2 wherein said at least one gas sensor is adapted to detect gas concentrations by diffusion of the gas to the sensing element.

5. The device of claim 1 wherein said means for monitoring includes means for transmitting signals from said at least one gas sensor to a data acquisition system.

6. The device of claim 5 wherein said means for  
5 transmitting signals includes an RF transmitter.

7. The device of claim 1 including at least one humidity sensor for monitoring humidity of atmosphere containing the concentrations of gas, an output of said at least one humidity sensor being used to supplement the output of said at least one  
10 gas sensor for humidity effects.

8. The device of claim 1 including means for drying gases before the gases reach said at least one gas detector.

9. A method by which the concentration of a gas, or the concentrations of a plurality of gases in a gas mixture, is  
15 measured, comprising the steps of:

(a) exposing a plurality of first gas sensors to a plurality of known gases to obtain voltage outputs from the sensors that together represent specific voltage profiles for each gas;

20 (b) storing the voltage profiles as a library in a software program;

(c) exposing a plurality of second gas sensors to an

unknown gas of unknown specific composition and measuring the voltage outputs from said plurality of second gas sensors to provide a voltage profile for the unknown gas; and

(d) using the software program to compare the voltage  
5 profile of the unknown gas to the voltage profiles of known gases in the library, and thereby determining the concentration of a specific gas or gases, in the unknown gas.

10 10. The method of claim 9 including oxidizing said known and unknown gases on a ceramic sensing element of each of said plurality of first and second gas sensors.

11. The method of claim 10 including housing said plurality of first gas sensors in an instrument comprising a flow-through sensor block with gas inlet and outlet ports for delivery of said known gases to said plurality of first gas sensors.

15 12. The method of claim 11 including pumping said known gases through the gas inlet and outlet ports.

13. The method of claim 12 including varying a load resistance for use of said plurality of first gas sensors across different concentration ranges of said known gases.

20 14. The method of claim 9 including locating said plurality of second gas sensors within a suit designed to provide a barrier

between a wearer and an external atmosphere.

15. The method of claim 14 wherein said plurality of second gas sensors exposed to the unknown gas produces signals that are transmitted to a data acquisition system.

5 16. The method of claim 9 including producing signals from said first and second gas sensors and transmitting the signals to a data acquisition system.

10 17. A method by which the concentration of an unknown gas, or the concentrations of a plurality of unknown gases in an unknown gas mixture, is measured within an article of protective gear, comprising the steps of:

a) providing at least one gas sensor within the article of protective gear so that the at least one gas sensor is exposed to the unknown gas within the protective gear;

15 b) providing a voltage output from the at least one gas sensor; and

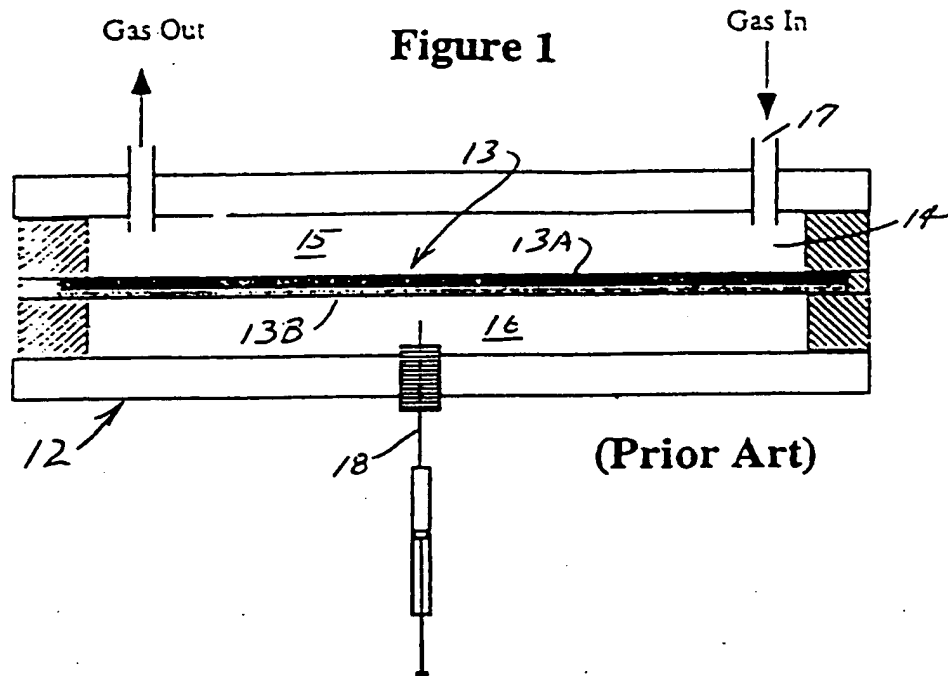
c) conveying the voltage output from the at least one gas sensor to a data acquisition system so as to compare the voltage output with data retained within the data acquisition system in  
20 order to define the unknown gas.

18. The method of claim 17 including the additional step of transmitting information with respect to the definition of the

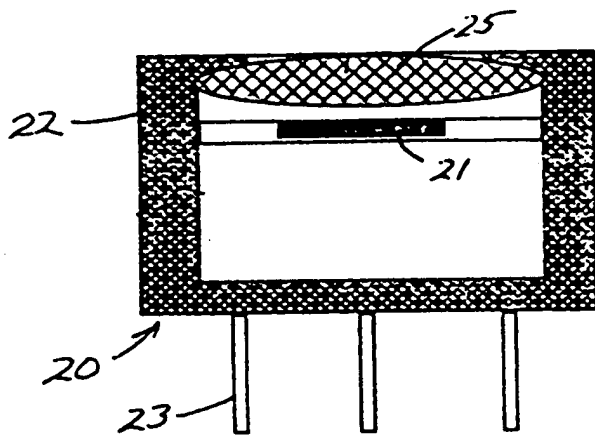
unknown gas to a signalling system.

19. A device for measuring concentrations of gases in a gas or gas mixture comprising; a housing, a plurality of gas sensors mounted within said housing, each of said gas sensors including a ceramic sensing element, electrical circuit means connecting each of said sensing elements to a source of power supply and for connecting an output from each of said sensing elements to a data acquisition system, a gas inlet into said housing such that gas enters said housing and into communication with said sensing elements and a gas outlet from said housing, and means for conveying the gas from said inlet to said outlet of said housing.

20. The device of claim 19 including a membrane associated with said gas inlet and being permeable only with respect to predetermined gases.

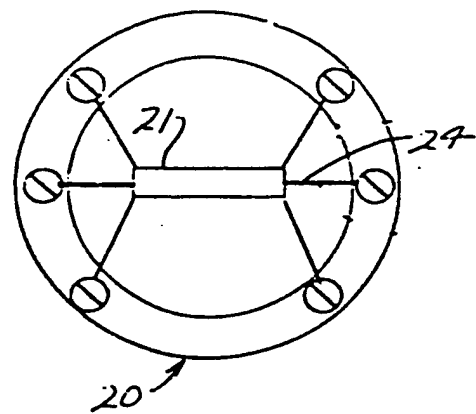


**Figure 2 A**



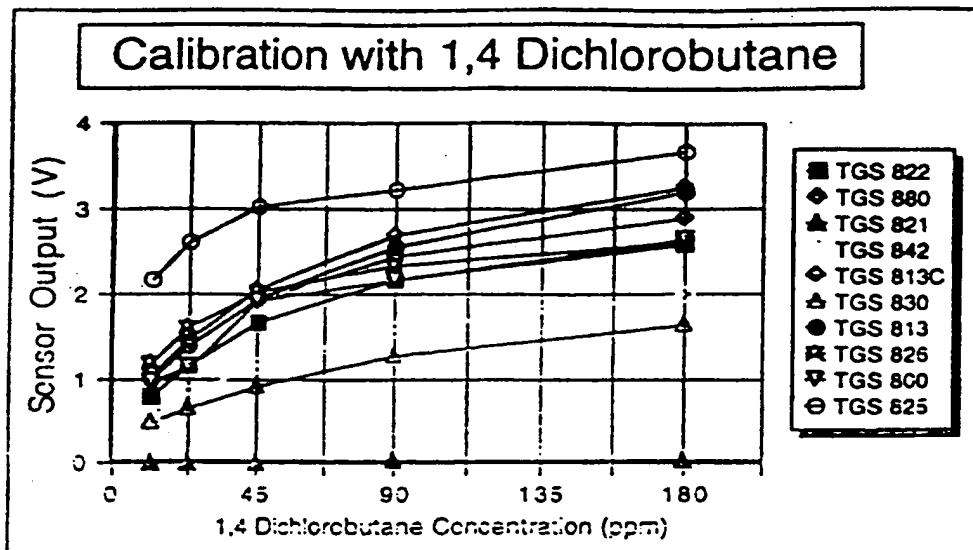
**(Prior Art)**

**Figure 2 B**



**(Prior Art)**

**Figure 7**  
**Calibration of Sensors with 1,4 Dichlorobutane**



**Figure 3**

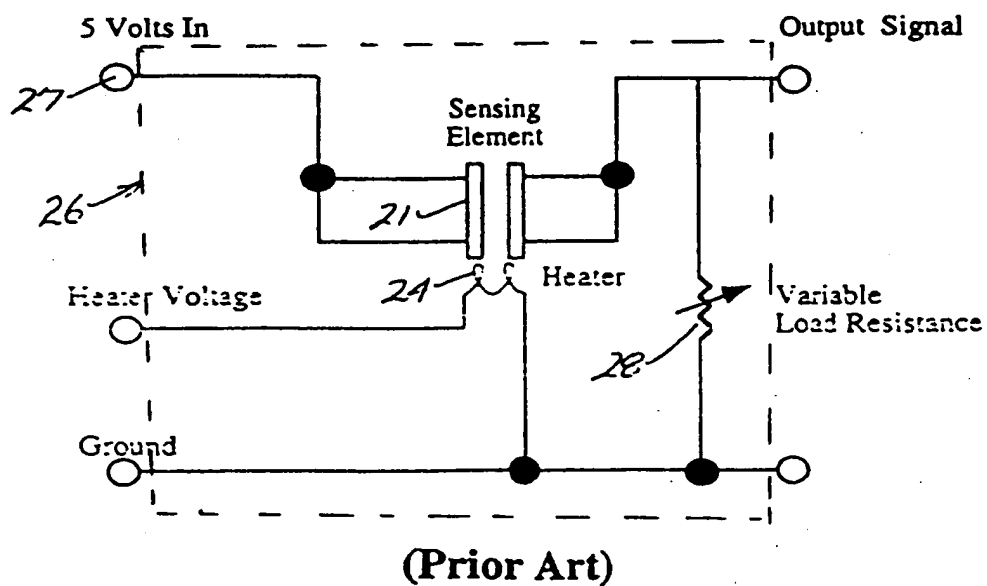
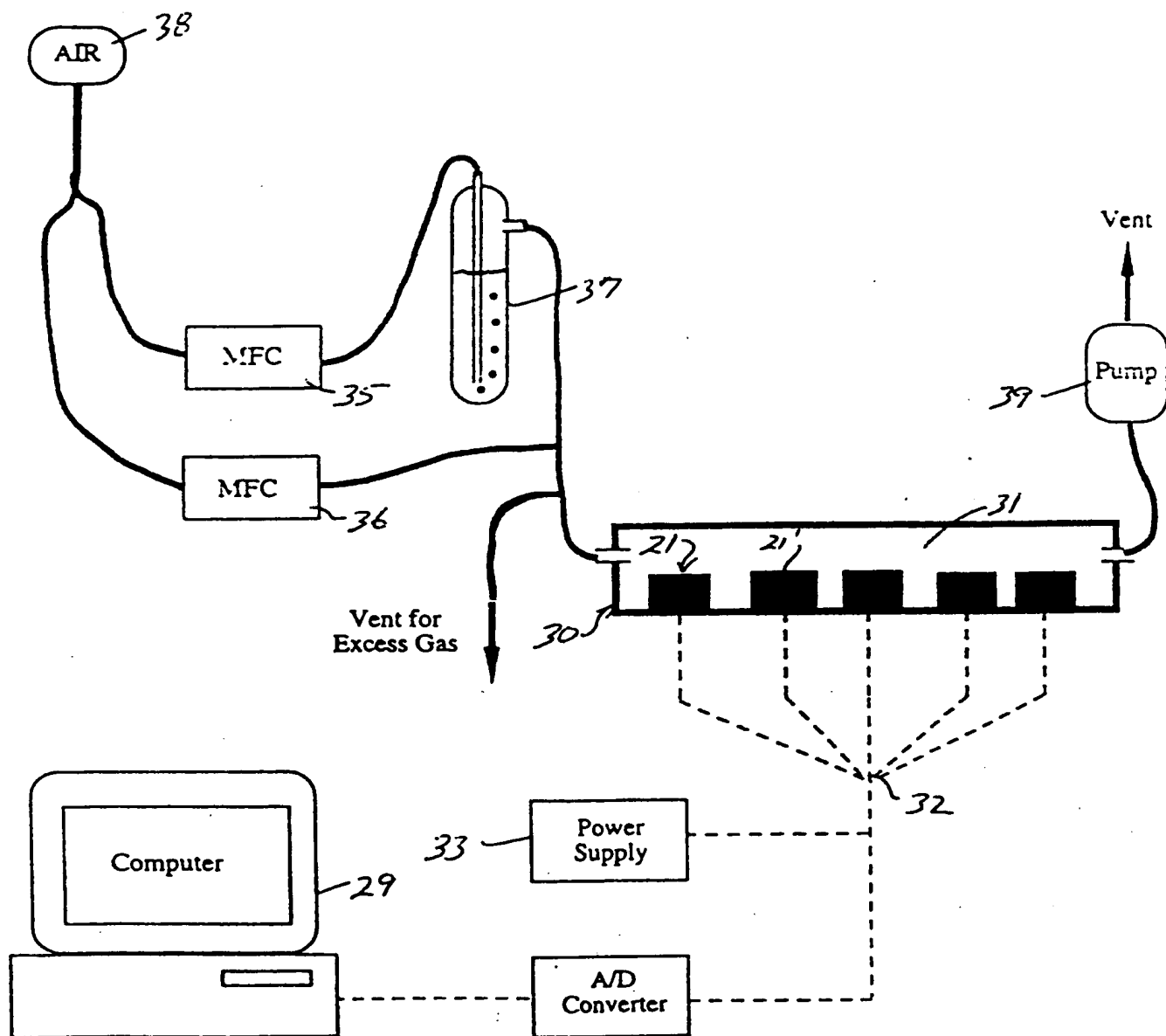
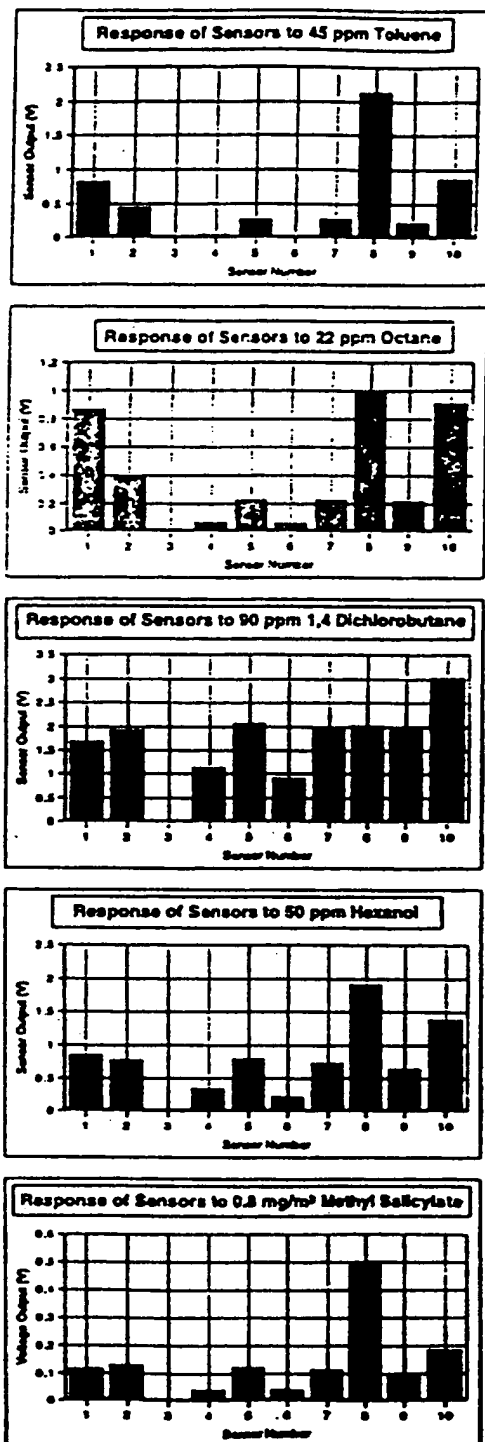




Figure 4



**Figure 5**  
**Sensor Responses to Test Gases**



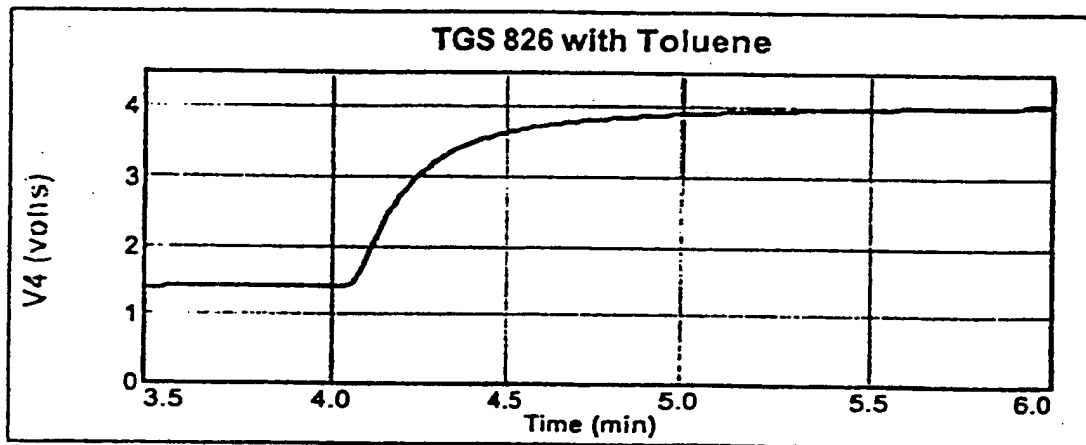
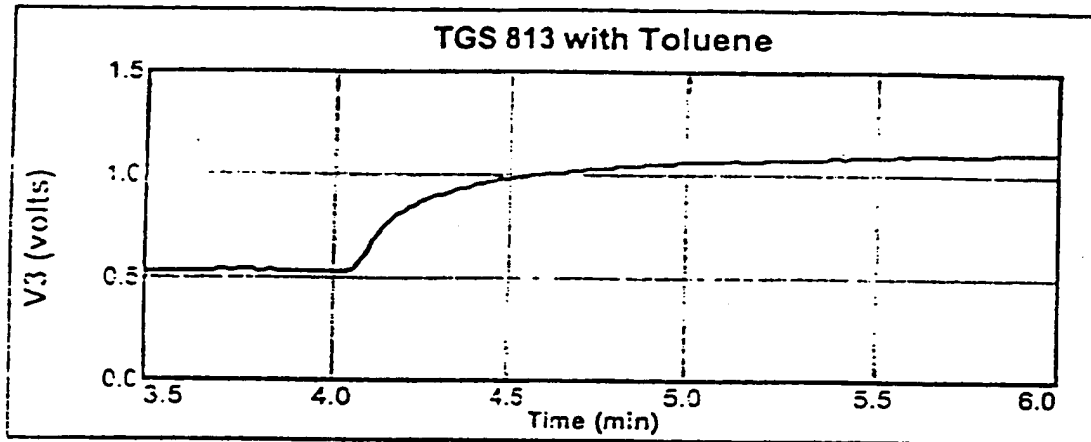
**Figure 6****Time Course of Gas Sensor Response to 180 ppm Toluene**

Figure 8

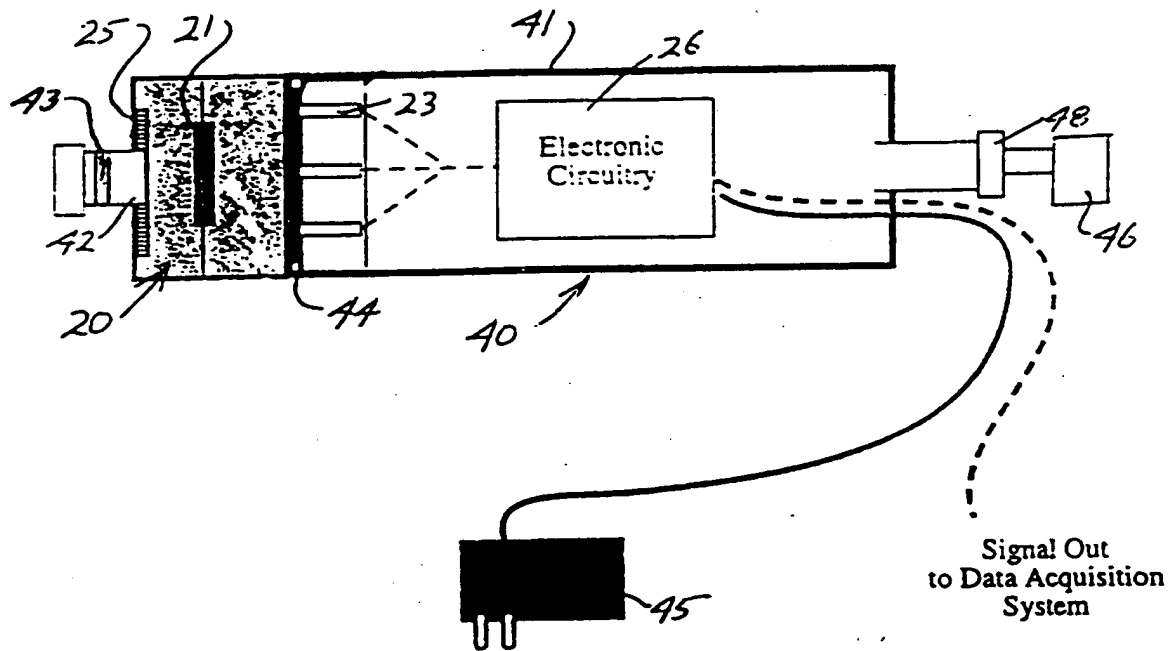
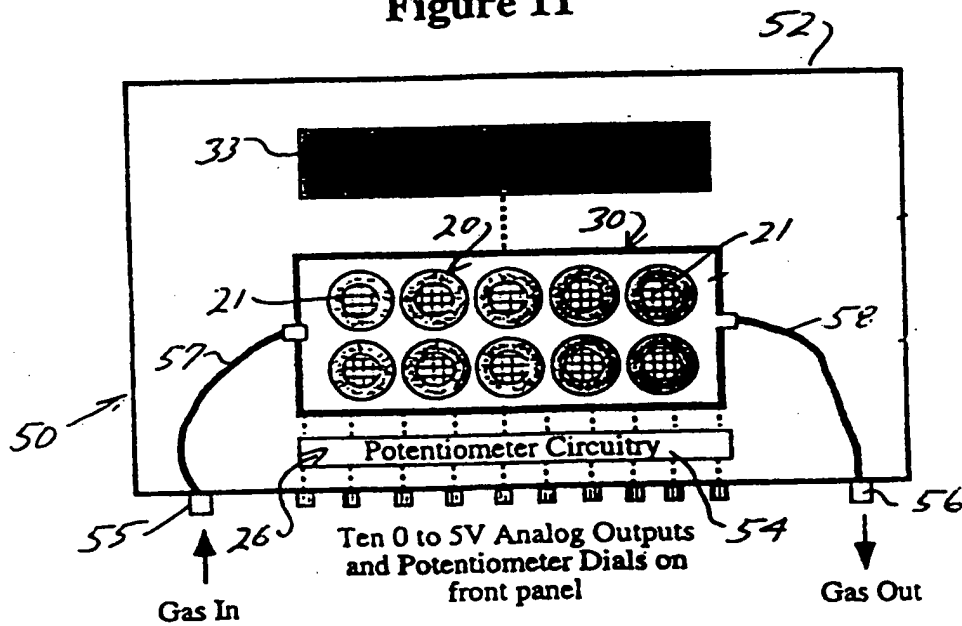


Figure 11



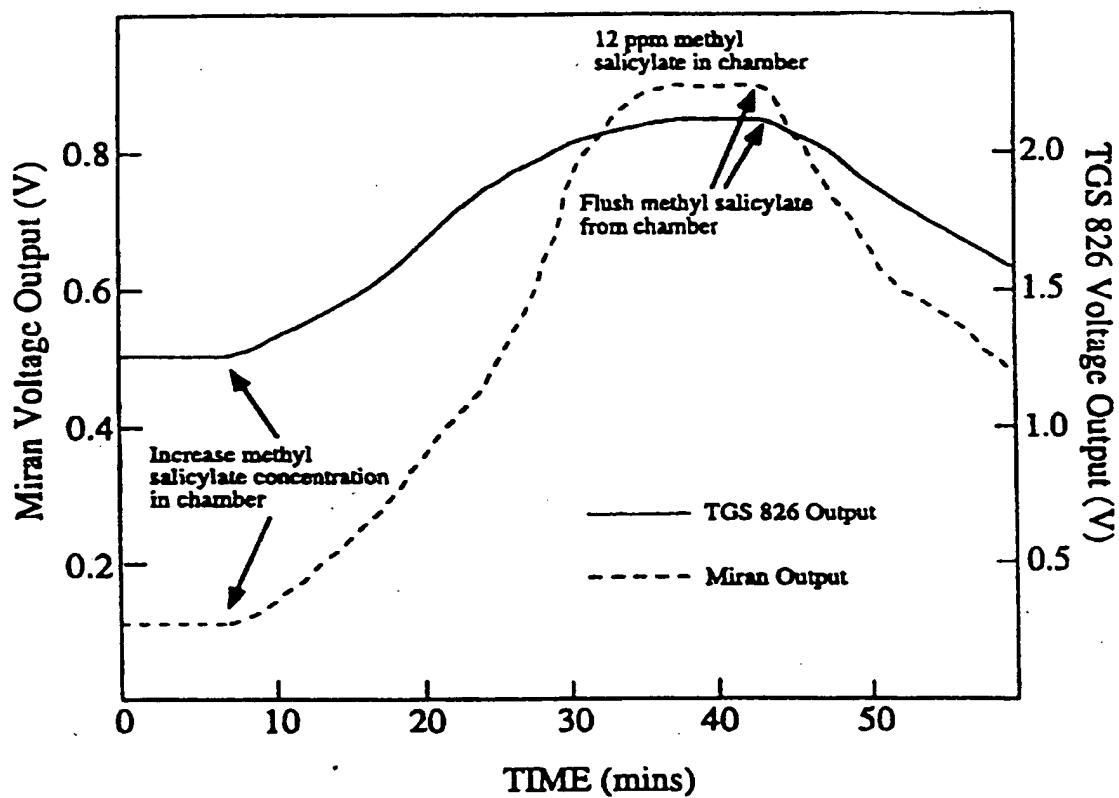
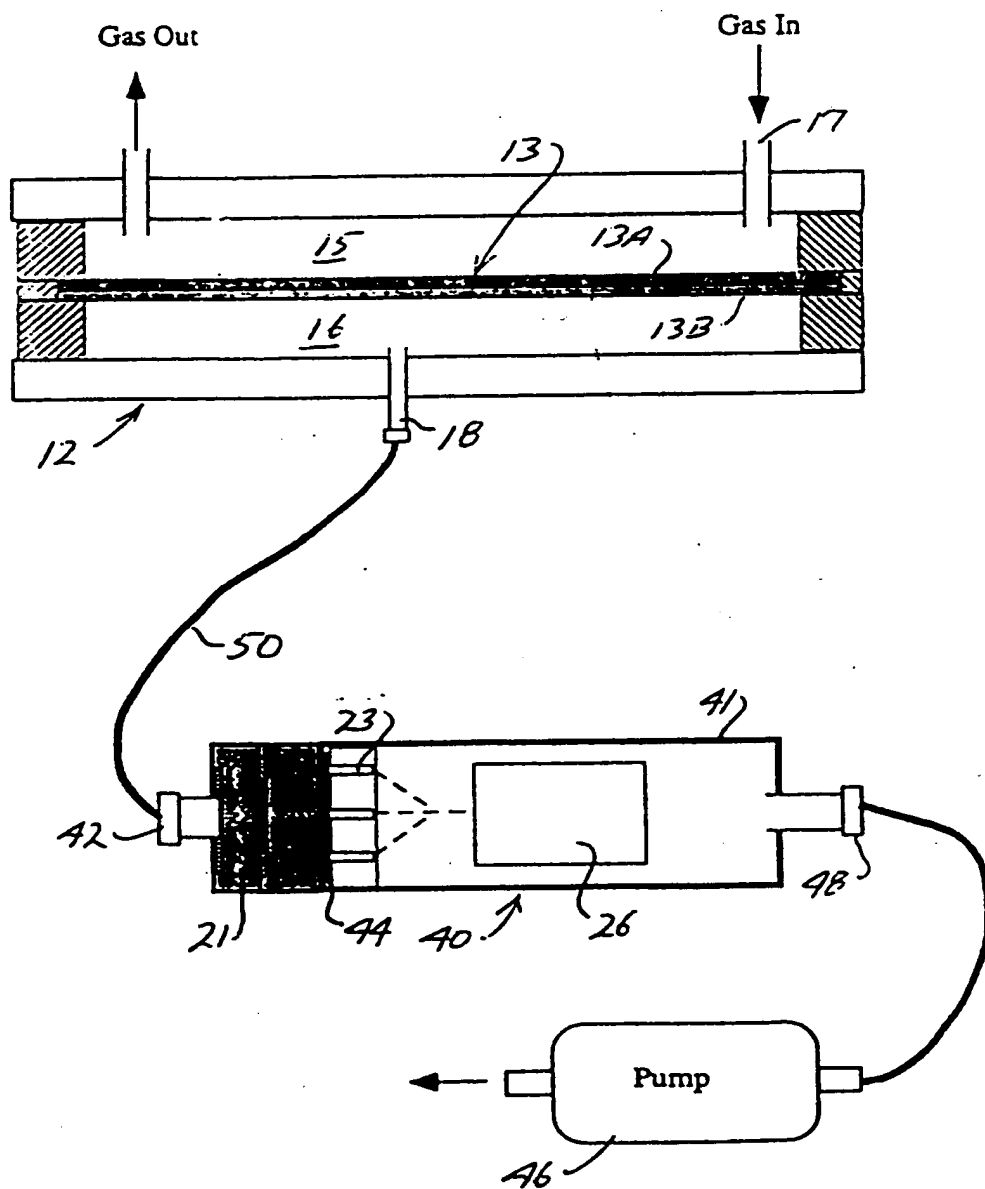
**Figure 9****Response of Gas Sensor TGS 826 and Miran Infra-Red Gas Analyser to Methyl Salicylate**

Figure 10



**Figure 12**

